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5.60 Thermodynamics & Kinetics  
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## **PARTITION FUNCTIONS**

The partition functions play a central role in statistical mechanics  
All the thermodynamic functions can be calculated from them!

Start with average system energy  $U = \langle E \rangle$

Substitute  $\beta \equiv 1/kT$

$$U = \langle E \rangle = \sum_i p_i E_i = \frac{1}{Q} \sum_i E_i e^{-\beta E_i}$$

Use the following result:

$$\left( \frac{\partial Q}{\partial \beta} \right)_{V,N} = \left( \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} \right)_{V,N} = - \sum_i E_i e^{-\beta E_i}$$

Then

$$\langle E \rangle = \frac{1}{Q} \sum_i E_i e^{-\beta E_i} = - \frac{1}{Q} \left( \frac{\partial Q}{\partial \beta} \right)_{V,N} = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = - \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} \left( \frac{\partial T}{\partial \beta} \right)_{V,N}$$

$$\left( \frac{\partial \beta}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{1}{kT} \right) = - \frac{1}{kT^2}$$

$$\boxed{U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}}$$

$Q(N,T,V)$  leads to natural connection with  $A(N,T,V)$

$$A = U - TS = U + T \left( \frac{\partial A}{\partial T} \right)_{V,N} \quad \text{using } dA = -pdV - SdT + \mu dN$$

$$\left( \frac{\partial (A/T)}{\partial T} \right)_{V,N} = \frac{1}{T} \left( \frac{\partial A}{\partial T} \right)_{V,N} - \frac{A}{T^2} = \frac{1}{T} \left( \frac{\partial A}{\partial T} \right)_{V,N} - \frac{U}{T^2} - \frac{1}{T} \left( \frac{\partial A}{\partial T} \right)_{V,N} = - \frac{U}{T^2}$$

$$U = -T^2 \left( \frac{\partial (A/T)}{\partial T} \right)_{V,N} = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$\Rightarrow \boxed{A = -kT \ln Q} \quad (\text{constant of integration can be taken to be zero})$$

All the other functions follow from  $U$  and  $A$

$$S = -\frac{A}{T} + \frac{U}{T} = k \ln Q + kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$p = -\left( \frac{\partial A}{\partial V} \right)_{T,N} = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

$$\mu = -\left( \frac{\partial A}{\partial N} \right)_{T,V} = -kT \left( \frac{\partial \ln Q}{\partial N} \right)_{T,V}$$

$$H = U + pV$$

$$G = A + pV$$

### Entropy in terms of microstate probabilities and degeneracies

$$\frac{S}{k} = \frac{U - A}{kT} = \frac{1}{kT} \frac{\sum_i E_i e^{-E_i/kT}}{Q} + \ln Q$$

But  $E_i = -kT \ln e^{-E_i/kT}$  so  $\frac{S}{k} = -\sum_i \frac{e^{-E_i/kT}}{Q} (\ln e^{-E_i/kT}) + \ln Q$

Since  $\sum_i p_i = \frac{\sum_i e^{-E_i/kT}}{Q} = 1$ , we can multiply  $\ln Q$  by 1 and combine terms to get

$$\frac{S}{k} = -\sum_i \frac{e^{-E_i/kT}}{Q} (\ln e^{-E_i/kT}) + \sum_i \frac{e^{-E_i/kT}}{Q} \ln Q = -\sum_i \frac{e^{-E_i/kT}}{Q} \ln \left( \frac{e^{-E_i/kT}}{Q} \right)$$

This is just

$$\boxed{S = -k \sum_i p_i \ln p_i}$$

Gibbs eq for  $S$  in terms of microstate probabilities

If the system is isolated, then all states have the same energy and the same probability  $p = 1/\Omega$  where  $\Omega$  is the number of degenerate states. Then

$$\boxed{S = k \ln \Omega} \quad \text{Boltzmann eq for } S \text{ in terms of degeneracy (his tombstone!)}$$

Can understand entropy in terms of disorder, or number of different available states. This microscopic picture of entropy is at the heart of statistical mechanics.

Even if system is not isolated, energy fluctuations are negligible for  $\sim 10^{24}$  molecules  $\Rightarrow$  can treat as if all states have the same energy, with equal probability  $\Rightarrow$  can use Boltzmann eq for  $S$

### Separation of partition functions

When can we write the canonical partition function as a simple product of molecular partition functions?

$$Q_{\text{trans}} = q_{\text{trans}}^N \quad \text{distinguishable particles}$$

$$Q_{\text{trans}} = q_{\text{trans}}^N / N! \quad \text{indistinguishable particles}$$

These hold when the system microstate energy  $E_i$  is a sum of independent molecule energies  $\varepsilon_i$  (denoted here by  $\varepsilon_{n_i}$  where  $n_i$  represent various quantum numbers for molecule  $i$ ).

$$E_i = \sum_{n_i} \varepsilon_{n_i} = \varepsilon_{n_1} + \varepsilon_{n_2} + \dots + \varepsilon_{n_N}$$

Then the sum over system microstate energies is just a sum over all the possible combinations of molecular energies  $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_N$

$$Q = \sum_i e^{-E_i/kT} = \sum_{n_1} \sum_{n_2} \dots \sum_{n_N} e^{-(\varepsilon_{n_1} + \varepsilon_{n_2} + \dots + \varepsilon_{n_N})/kT}$$

$$= \left( \sum_{n_1} e^{-\varepsilon_{n_1}/kT} \right) \left( \sum_{n_2} e^{-\varepsilon_{n_2}/kT} \right) \dots \left( \sum_{n_N} e^{-\varepsilon_{n_N}/kT} \right) = q_1 q_2 \dots q_N = q^N$$

And for indistinguishable particles that can interchange positions,  $1/N!$  corrects for overcounting of indistinguishable system states

So if system energy = sum over independent molecular energies  $\Rightarrow$   
 Canonical partition function = product of molecular partition functions

Same approach for molecular partition function:

If molecular energy = sum of independent degree of freedom energies  $\Rightarrow$   
 Molecular partition function = product of degree of freedom partition functions

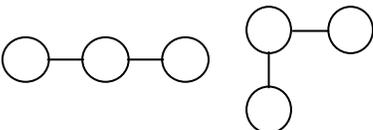
e.g. molecular energy  $\varepsilon$ :  $\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} + \dots$

$\Rightarrow$  molecular partition function  $q$ :  $q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \dots$

For a polymer in a liquid,  $\varepsilon \approx \varepsilon_{(\text{everything else})} + \varepsilon_{\text{conf}} \Rightarrow q \approx q_{(\text{everything else})} q_{\text{conf}}$

$\Rightarrow$  can calculate  $\varepsilon_{\text{conf}}$  &  $q_{\text{conf}}$  even if other properties are hard to determine

Example: Molecules with 2 distinct configurations of  $\sim$  same energy  $\varepsilon_{\text{conf}} = 0$

e.g.   $\Rightarrow q_{\text{conf}} = g_{\text{conf}} = 2$

Calculate molecular & canonical partition functions  $q$  &  $Q$  including translation

Lattice model for translation:

$N$  molecules in the gas phase

Molecular volume =  $v$ , Total volume =  $V$

All molecular positions have equal energy  $\varepsilon_{\text{trans}} = 0$

$$q_{\text{trans}} = g_{\text{trans}} = V/v$$

$$q = q_{\text{conf}} q_{\text{trans}} = 2V/v$$

$$Q_{\text{trans}} = (q_{\text{trans}})^N / N! = (V/v)^N / N!$$

$$Q_{\text{conf}} = (q_{\text{conf}})^N \text{ (No } 1/N! \text{ factor needed - configurational states not overcounted)}$$

$$Q = Q_{\text{conf}} Q_{\text{trans}} = (q_{\text{conf}})^N (q_{\text{trans}})^N / N! = 2^N (V/v)^N / N! \approx 2^N (10^{30})^N / N!$$

Could extend to include rotation, vibration, other degrees of freedom

